



Supramolecular polymers at work

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Sophisticated polymeric materials with 'responsive' properties are beginning to reach the market. The use of reversible, noncovalent interactions is a recurring design principle for responsive materials. Now, recently developed hydrogen-bonding units allow this design principle to be taken to its extreme. Supramolecular polymers, where hydrogen bonds are the only force keeping the monomers together, form materials whose (mechanical) properties respond strongly to a change in temperature or solvent. In this review, we describe the developments that have led to hydrogen-bonded supramolecular polymers and discuss the use of these materials in advanced applications.

In the past 60 years, polymers have revolutionized our lives. Their low price, high processability, and exceptional mechanical properties have led to the use of polymers in ever more sophisticated applications. Presently, a strong scientific interest in 'smart' polymers – polymers that respond to changes in temperature, solvent, or the presence of 'signal' chemicals – is beginning to expand the potential field of applications for such materials even further.

Key to the responsiveness of smart materials is the reversibility of the noncovalent interactions that lead to the change in properties. In nature, responsive structural polymers abound and their capacity to respond is often brought about by reversible assembly/disassembly. Scaffolds, such as those that constitute the cellular skeleton, are formed only where and when they are required, and they are disassembled into small building blocks when their task has been fulfilled. As opposed to a purely macromolecular approach, such a modular, supramolecular strategy allows a fast and efficient response to changing needs in the cellular cycle.

The field of supramolecular chemistry has been developed over the past 25 years by synthetic chemists, inspired by the ubiquity of reversible, yet highly specific, intermolecular processes in nature. Supramolecular polymers form the most recent branch in the tree of 'chemistry beyond the covalent bond', as supramolecular chemistry is sometimes called. Despite their short history, supramolecular polymers are already beginning to find commercial use in applications that take advantage of the reversibility and responsiveness of noncovalent interactions.

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Introduction

Before macromolecules were generally accepted, the majority of scientists were convinced that polymer properties were the result of the colloidal aggregation of small molecules or particles. It was only after the pioneering work of Staudinger¹ that it became evident that polymeric properties in both solution and the solid state are the result of the macromolecular nature of the molecules. A large number of repeating units are covalently linked into a long chain and the entanglements of the macromolecular chains are responsible for many typical polymer properties.

The impressive recent progress in supramolecular chemistry has paved the way for the design of polymers and polymeric materials that lack macromolecular structure. Instead, highly directional secondary interactions are used to assemble the many repeating units into a polymer array. Polymers based on this concept hold promise as a distinctive class of novel materials because they combine many of the attractive features of conventional polymers with the reversibility originating from the secondary interactions. Consequently, the architectural and dynamic parameters that determine polymer properties, such as the degree of polymerization, lifetime of the chain, and its conformation, can be reversibly adjusted, resulting in unique materials that respond to external stimuli. These aspects of supramolecular polymers have led to a recent surge in attention for this promising class of compounds and have stimulated us to bring together materials science and supramolecular chemistry. Fig. 1 shows the required directionality in supramolecular interactions compared with the historical and current macromolecular view on polymers.

What are supramolecular polymers?

Loosely defined, supramolecular polymers are those in which the monomers are held together by noncovalent interactions². In all condensed molecular materials, whether they are liquid, glassy, or (liquid) crystalline, noncovalent interactions with little specificity or directionality are present. However, when highly directional forces dominate the interaction between neighboring molecules, long chains or networks of concatenated molecules can be formed, resulting in many of the (mechanical) properties that have made polymeric materials so successful. Long chains, which lead to polymer-like behavior, are only formed when the interactions between the monomeric units are strong enough.

The presence of linear chains, which persist when a material is heated or dissolved, is the hallmark of a successful design of strong and directionally interacting functionalities. In a fundamental research context, where the goal is to understand the relation between molecular structure and macroscopic properties, strength and directionality are of prime importance³. While the directionality and strength of the interactions between monomers are also important when developing applications for supramolecular polymers, there are additional requirements that have to be met for the successful application of these materials. The most challenging of these requirements have been synthetic availability, cost, and stability of appropriate functionalities.

Quadruple hydrogen bonds aka UPy

Hydrogen (H) bonds hold a prominent place in supramolecular chemistry because of their directionality and versatility, although they are not among the strongest noncovalent interactions. Cooperativity holds the answer to this problem and, consequently, several systems have been designed that combine multiple H-bonds in a row. Indeed, this increases the strength of the interaction and, moreover, enhances its specificity. Very stable complexes can be obtained when quadruple H-bonding units are employed. Therefore, it was not until the development of the quadruple H-bond unit by Meijer and Sijbesma^{4,5} that H-bonding systems were developed with sufficiently high association constants to allow the formation of supramolecular polymers with significant degrees of polymerization. These self-

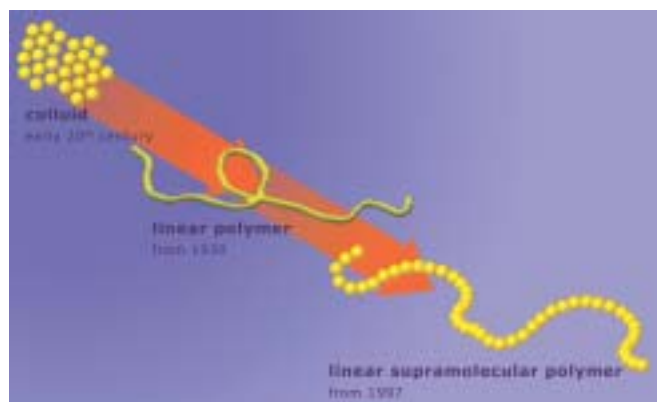


Fig. 1 Schematic representation of the evolution in time of macromolecular science from colloids, via the original work of Staudinger¹ (who showed, for the first time, that high molecular weight linear polymers do exist), to supramolecular polymers that can be seen as a combination of both earlier concepts: a high molecular weight linear polymer held together by secondary interactions. (Reproduced with permission of SupraPolix BV.)

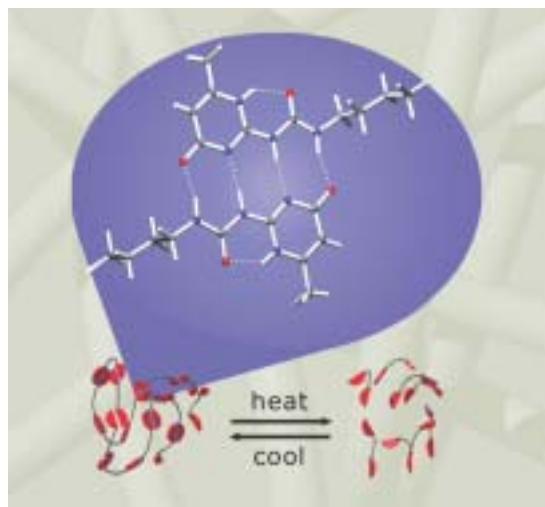


Fig. 2 Schematic representation of a linear supramolecular polymer. Enlargement shows a representation of the X-ray structure of the H-bonded dimer of the UPy group that holds the supramolecular polymers together. (Reproduced with permission of SupraPolix BV.)

complementary quadruple H-bonding units based on 2-ureido-4[1H]-pyrimidinones (Fig. 2) dimerize in toluene with an association constant of $K_{\text{dim}} = 6 \cdot 10^8 \text{ M}^{-1}$ and a lifetime of 1.7 s. Application of these H-bonding units as associating end-groups in di- or multifunctional molecules has resulted in the formation of supramolecular polymers with high degrees of polymerization (DP). The development of the ureidopyrimidinone (UPy) functionality, a synthetic H-bonding unit with a very high association constant, has helped enormously in opening the way for the exploration of all aspects of supramolecular polymers.

Supramolecular polymers with UPy

The difunctional UPy compound shown in Fig. 2 can easily be made in a one-step procedure from commercially available compounds (hexyldiisocyanate and methylisocytosine). The high association constant of UPy combined with its difunctional nature results in the formation of a stable and

long polymer chain in solution as well as in the bulk. Dissolving a small amount of this low molecular weight compound in chloroform gives solutions with high viscosities.

The bulk viscoelastic properties of low molecular weight, bifunctional UPy compounds have been studied using dynamic mechanical thermal analysis (DMTA), rheology, and dielectric relaxation spectroscopy⁶. One of the salient features of the materials, with great relevance for applications, is the extremely high activation energy for viscous flow of 105 kJ/mol. This results in a strongly temperature dependent melt viscosity, which increases processability of these materials at temperatures only moderately higher than the melting point or T_g . The high activation energy can be attributed to the contribution of three mechanisms to stress relaxation in sheared melts of supramolecular polymers. Firstly, a mechanism shared with covalent polymers, in which they escape from entanglements by reptation. In addition to that, supramolecular polymers have enhanced relaxation at higher temperatures because the chains become shorter. Finally, in a mechanism unique to reversible polymers, the supramolecular chains lose strain by breaking, followed by recombination of free chain ends without strain. Breaking rates increase with temperature, and contribute to the temperature-dependent behavior of supramolecular polymers.

Supramolecular materials

The quadruple H-bonded unit has been further employed in the chain extension of telechelic polysiloxanes, polyethers, polyesters, poly(ethylene/butylenes), and polycarbonates⁷. In these compounds, the material properties have been shown to improve dramatically upon functionalization, resulting in materials that combine many of the mechanical properties of conventional macromolecules with the low melt viscosity of low molecular weight organic compounds (Fig. 3).



Fig. 3 Illustration of the phase changes in a rubbery material based on Kraton®, (poly(ethylene-co-butylene), modified with UPy, exemplifying the diversity in phase behavior because of the supramolecular interactions. (Reproduced with permission of SupraPolix BV.)

The reversibility of supramolecular polymers adds new aspects to many of the principles that are known from condensation polymerization. For example, a mixture of different supramolecular monomers will yield copolymers, but it is extremely simple to adjust the copolymer composition by adding an additional monomer. Moreover, the use of monomers with a functionality of three or more will give rise to network formation. However, in contrast to condensation networks, the 'self-healing' supramolecular network can reassemble to form the thermodynamically most favorable state, thus forming denser networks (Fig. 4).

Applications of supramolecular polymers

The strong secondary interactions of the quadruple H-bonding unit, combined with the ease of synthesis, is probably the main reason that, following the first publication in 1997 by Sijbesma *et al.*⁵, there have been numerous patent applications filed using supramolecular architectures in fields ranging from adhesives⁸, printing⁹⁻¹³, cosmetics^{14,15}, personal care¹⁶, to coatings¹⁷. The added value that supramolecular polymers are foreseen to give to these everyday applications is based on their improved processing in the melt or solution while maintaining excellent material properties in the solid state, the lower temperatures needed to obtain tractable materials, the ease of synthesis, the compatibility with existing polymeric systems, and the intrinsic reversibility of supramolecular systems that makes the materials easily removable. In this section, several examples of these

applications will be discussed that take advantage of the possibilities originating from the unlocking of the processing properties from the material properties by using supramolecular interactions. Moreover, this unambiguously shows that supramolecular polymers are not restricted to the laboratory anymore.

Ink-jet inks

An application in which the dramatic differences in phase behavior of supramolecular polymers in a relatively narrow temperature range can be used is ink-jet printing. In this application, images are created on a substrate (i.e. paper) by the ejection of ink droplets through a small orifice. The ink, therefore, has to be low viscosity in order to be ejected in small droplets. On the other hand, the ink needs to be highly viscous, almost a solid, once the droplet hits the paper – otherwise, the ink will smear out through capillary action of the paper, resulting in blurry pictures.

Xerox has filed two patents in which supramolecular polymers are used as binders in ink compositions. One application relates to hot-melt inks⁹, consisting of a colorant and a binder. These inks are solid at temperatures below 50°C and a liquid with a viscosity of around 20 cps at 160°C. The binder is a multifunctional low molecular weight compound that has been functionalized with two to five UPy groups, resulting in polyether compounds that form supramolecular networks. Mixing these materials at elevated temperatures with other ingredients like (UV) ultraviolet-stabilizers, antioxidants, and colorants results in inks that can be used in hot-melt ink printers.

In the other patent application filed by Xerox¹⁰, aqueous based inks are formulated with supramolecular polymers. The material properties of the ink (i.e. viscosity) are, in this case, tuned with the heat and polarity of the solvent medium, since these parameters determine the amount of H-bonding between the different UPy groups. The ink consists of an aqueous solvent, colorant, and supramolecular polymeric additive. Because of the high polarity of the solvent, H-bonding is strongly reduced in the ink solution, resulting in a rather low viscosity. In contrast, the viscosity of the ink rapidly increases during jetting as the solvent evaporates from the droplet, which, together with a temperature drop in the ink, results in a virtual increase of molecular weight of the polymer additive because of the formation of H-bonds. Consequently, the ink is prevented from spreading on the paper and a clear image with good permanence

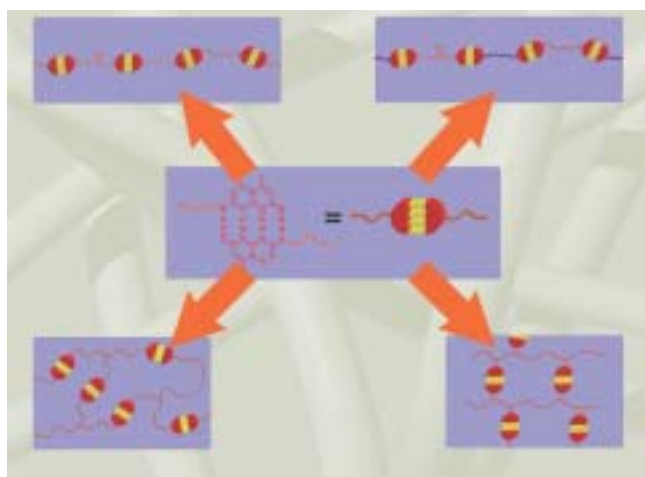


Fig. 4 Different architectures possible for supramolecular polymers. Top left: linear supramolecular polymer. Top right: linear supramolecular block-copolymer. Bottom left: supramolecular network via branching. Bottom right: supramolecular network via grafting. (Reproduced with permission of SupraPolix BV.)

characteristics is produced. The supramolecular compounds used in this application are comparable to the ones for hot-melt ink, the only difference is the formulation, which contains around 10% solids (binder, pigment or dye, and surfactant) in the aqueous solvent. Interestingly, Agfa-Gevaert in Belgium has filed a patent related to ink-jet inks in which the dyes themselves have been modified with UPy groups, resulting in an improved lightfastness of the ink¹¹.

Printing plates

Another way to use supramolecular polymers is shown in a patent application filed by Kodak Polychrome Graphics¹², which takes advantage of the fact that the solubility of supramolecular polymer coatings increases after heating (thermal solubilization). This concept is applied in printing plates that are used in lithographic printing processes. Lithographic printing is based on the immiscibility of hydrophobic ink and water; the printing plate consists of hydrophilic surfaces that are wetted by the water and hydrophobic surfaces that are wetted by the ink. In this way, hydrophobic patterns on the printing plate can be transferred to a substrate (i.e. paper) to create an image. Typically, patterns are created by using a radiation-sensitive coating, which becomes soluble upon exposure to radiation and can be removed in a subsequent developing process to reveal the hydrophobic surface underneath that will absorb the ink (positive-working printing plate). If the top layer is made insoluble by exposure to radiation, and the unexposed areas are removed in developing, a negative-working printing plate is obtained.

In these patent applications, a thermally imageable, positive-working printing plate is disclosed that makes use of a supramolecular polymer as a thermally sensitive coating. The polymers used are obtained by reacting polyfunctional resins (phenolic, acrylic, or polyester) with isocyanate functional UPy. Specific examples of resins are phenol/cresol novolaks and 4-hydroxy-styrene/styrene copolymers. The resulting coating consists of these supramolecular cross-linked polymers and (IR) infrared-dyes that transform laser light into heat. Because the resins contain several reversible cross-links to reinforce the coating, it is possible to disrupt these cross-links thermally with short (~100 μ s) IR laser illumination and solubilize the exposed regions in the following developing step. This procedure eliminates two processing steps normally used in preparing printing plates (preheating and post-development baking), and superior

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Initial work in the field of supramolecular polymer chemistry, performed by the group of Bert Meijer and Rint Sijbesma at the University of Technology in Eindhoven, The Netherlands, has led to the development of new materials combining the sophisticated use of self-organization with strong noncovalent interactions. The key to their success is the use of quadruple H-bonding units that combine easy preparation with strong secondary interactions. Great interest from industry in the concept of reversible polymers was one of the main motivations to start SupraPolix. SupraPolix develops materials containing supramolecular polymers, thereby offering a new concept in the world of plastics by separating the processability demands from the material demands: incorporation of even a small amount of a UPy group in existing plastics dramatically simplifies the processing. As a consequence, production can be cheaper and faster, while the consumer will benefit from innovative products that are easier to use. The reduced energy consumption during processing and the improved recycling of these materials makes the technology environmentally benign. Implementation of the technology will allow producers to comply with the environmental constraints of the near future without any concession to the quality of the material.

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press-life is obtained when compared with other digitally imaged compositions.

Polymerization-induced phase separation

The dynamic flexibility of supramolecular polymers is being exploited by Keizer and coworkers in polymerization-induced phase separation (PIPS) with H-bonded supramolecular polymers¹⁸. In PIPS, a polymer is dissolved in a reactive monomer, which is subsequently polymerized to cause phase separation, resulting in two polymeric phases with certain morphology (Fig. 5). PIPS is currently used to produce multiphase composite materials like high-impact polystyrene, avoiding the use of solvent and consequently resulting in fast and clean production of polymeric materials.

The rate of phase separation in PIPS is generally limited by the mobility of the dissolved polymer. Supramolecular polymers, however, may dissociate when dissolved in a

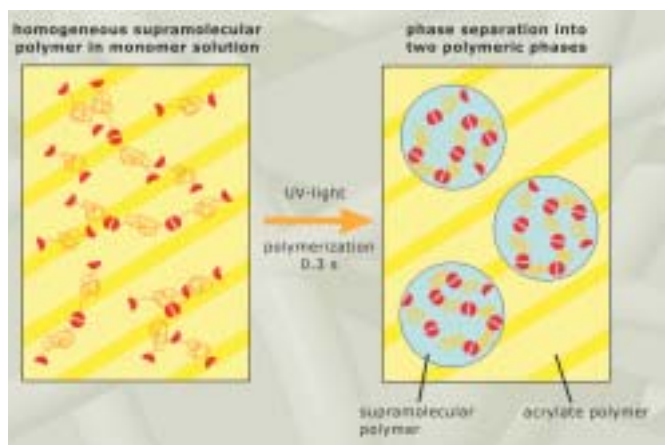


Fig. 5 Schematic representation of PIPS using H-bonded supramolecular polymers: the situation before polymerization of the acrylate-monomer is depicted on the left and the situation after the polymerization of the acrylate monomer, which has induced phase separation, is depicted on the right.

reactive monomer, resulting in strongly enhanced diffusion. Hence, macroscopic phase separation of supramolecular polymers can be reached within a very short reaction time.

Keizer *et al.*¹⁸ report the PIPS of solutions of H-bonded supramolecular polymers in acrylates, within the short reaction times (0.3 s) used in UV-curing. The cured films are colorless, transparent, flexible, and show macrophase separation in secondary electron microscopy. Moreover, their mechanical behavior is comparable to high molecular weight polymers. Interestingly, DSM has filed a patent that describes the use of supramolecular polymers in coatings for glass fibers¹⁷, a process which needs very fast reaction times indeed. In addition, this strategy could be used for either stratification or patterning via a mold in thin films.

Outlook and the modular approach

Ten years ago, the first supramolecular polymers were seen as scientific curiosities. Now this field of research is generating several technologically important applications. Progress in supramolecular chemistry has made it possible to assemble small molecules into polymer arrays, and the created structures possess many of the well-known properties of 'traditional' macromolecules. Because of the reversibility in the bonding, these supramolecular polymers are under thermodynamic equilibrium and their properties can be adjusted by external stimuli.

H-bonded systems are now being shown to be of technological relevance instead of just a scientific curiosity. A large variety of applications are feasible, especially since the chosen approach can also be used for the modification of telechelic oligomers or to modify existing polymers. A highly interesting outlook for supramolecular polymers is the option of the modular approach. By having a 'box' of different and functional UPy-based building blocks, it should be possible to create new functions by just mixing the building blocks in the appropriate amounts. These materials could be formed by self-assembly and changed by adding another component. Therefore, the possibility of tuning the properties by changing the relative ratio of UPy-monomer in the copolymer feed seems very attractive, while hybrids between blocks of macromolecules and supramolecular polymers would be easy to prepare. Novel thermoplastic elastomers, superglues, hot-melts, and tunable polymeric materials are within reach and are currently receiving a great deal of attention from several industrial research labs. **MI**

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